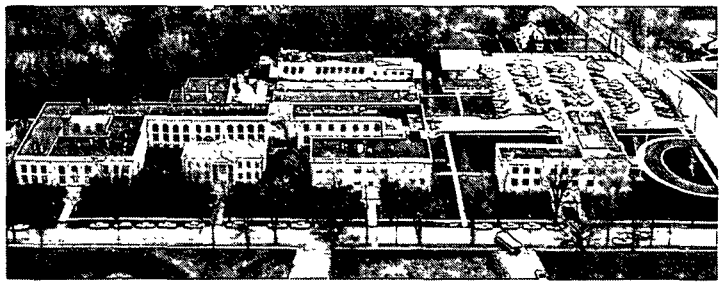

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THE APPLICATION OF NEGATIVE CHEMICAL IONIZATION MASS SPECTROSCOPY TO THE ANALYSIS OF PULP AND PULPING LIQUOR EXTRACTS

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THE APPLICATION OF NEGATIVE CHEMICAL IONIZATION MASS SPECTROSCOPY TO THE ANALYSIS OF PULP AND PULPING LIQUOR EXTRACTS

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ABSTRACT

The pulp and liquor extracts from soda, kraft, and soda/anthraquinone (AQ) pulping of loblolly pine were analyzed directly and after methylation by gas chromatography-mass spectroscopy (GC-MS). Three types of MS were employed: electron impact, and positive and negative chemical ionization. The latter technique was quite sensitive to sulfur components (kraft) and AQ and AQ derivatives (soda/AQ). The principal components of the extracts were resin and fatty acids; however, the detailed GC-MS analysis also showed the presence of lignin fragments, oxidized resin acids, dehydrodehydroabietic acid, and 10-methylene-, 10-hydroxymethyl- and 10-formyl-anthrone. The latter anthrones appear to be intermediates in the conversion of AQ + carbohydrates to 10-methyl-anthrone. Negative chemical ionization spectra were recorded for several known lignin-related components and AQ derivatives.

INTRODUCTION

Various analytical techniques have been applied to the analysis of pulps and pulping liquors for anthraquinone (AQ) and AQ by-products.[1-12] We describe here the value of negative chemical ionization (NCI) mass spectroscopy (MS) as a technique in the analysis of soda, kraft, and soda-AQ pulping extracts. This technique is compared with two other modes of obtaining mass spectral

data, namely, electron impact (EI) and (positive) chemical ionization (CI).

A characteristic feature of EI-MS is the production of numerous fragment ions as a result of the collision of a high-energy electron with the sample.[13] In CI-MS the high-energy electrons principally collide with a reagent gas, such as methane, to give positively charged reagent gas ions and low-energy ("thermal") electrons.[14] The former can (a) add to sample molecules to give M + H, M + C_2H_5 and M + C_3H_5 positive ions and (b) abstract functional groups to give fragment ions, such as M-OH.[15] The thermal electrons can add to certain sample molecules to give negative ions (M^-).[16] Depending on the polarity of the mass spectrometer's focusing and detecting systems either the positive or negative ions can be detected.

Only certain types of molecules, those having low level unoccupied molecular orbitals, will accept thermal electrons. Thus, NCI-MS has a specificity which is quite different from the EI and CI modes. For example, extended conjugated, electronegatively substituted aromatics are highly sensitive.[16] Anthraquinone and its derivatives fit into this class and should be readily detected by NCI-MS, as AQ is by electron-capture GC.[10]

Our study was limited to the analysis of pulp and liquor extracts and, therefore, limited to chloroform-soluble, volatile substances. The black liquor soluble lignin material which binds considerable amounts of AQ (derivatives)[5,6,12] was not analyzed.

RESULTS AND DISCUSSION

Samples of loblolly pine chips were pulped under soda, kraft, and soda/AQ conditions to similar kappa numbers. The pulps were separated from the "strong" liquor, disintegrated, washed with water ("weak" liquor), and extracted with chloroform. A portion of $CHCl_3$ extracts was methylated with diazomethane. The strong and weak liquors were handled separately. After acidification,

the liquors were partitioned between a polar and a nonpolar solvent pair. Evaporation of the nonpolar solvent gave principally tall oil components, a portion of which was methylated.

The assignment of structures to the main components in each MS-analyzed sample generally proceeded in the following manner. First, the EI spectra were recorded (stored in computer memory) and then compared with the EI spectra of roughly 50,000 known compounds stored in the mass spectrometer's "software." This comparison either provided the structure with a high degree of confidence or provided insights into possible structures. Second, the data from the EI run were compared with those from the CI run, which often provided reliable molecular weight and supplemental structural information. Third, the spectral fragmentation patterns were examined to ascertain if the assigned structure was consistent with the other data. Finally, to a limited extent, the mass spectra and GC retention time of known, available samples were compared with components observed in the extract analyses.

The EI GC-MS spectra of strong and weak liquors were so similar that further analysis of the latter was not pursued. The purpose of analyzing both methylated and unmethylated samples was as another aid in interpretation; the GC retention time of acidic components will differ in the two types of samples, exposing different retention time regions. In general, the GC-MS of unmethylated samples did not, however, provide much additional information. The exception was the more convenient analysis of the low retention time lignin fragments, including vanillin, vanillic acid, acetovanillone, 1-aryl-1-propene,-ethane,-2-propanone,-3-propanal,-2-hydroxyethane,-acetic acid, and 1,2-diarylethane (aryl ≡ 4'-hydroxy-3'-methoxyphenyl).

Except for some differences in relative intensities, the components in the pulp-extracted samples were the same as the principal resin and fatty acids components in the corresponding liquor extracts. The only lignin fragments observed were vanillin and acetovanillone. Since one does not know how to judge small

differences in component intensities - real or an artifact of extraction efficiencies, we learned little from the pulp extracts.

Basically, this brings us to comparing methylated strong liquor extracts. Figures 1-3 display the EI, CI, and NCI spectra of each of the pulping liquor extracts. The GC carrier gas for the CI runs was methane, whereas it was helium for the EI runs. This fact, together with different day analyses, explains why the GC retention times were not a perfect match in some cases. The peak profiles for both the EI and CI runs for each extent were basically identical. On the other hand, the NCI spectra in each case were quite distinctive, indicative of the specificity of this technique. The major components in the samples were transparent in NCI and only minor, electron-capture type components appeared.

A comparison of the EI (or CI) runs of the three pulping extracts showed some differences in intensities, but basically the same kinds of components. The kraft liquor had an extra signal at 7.9-minute retention time which was attributed to a methyl octadecadienoate. The variable intensity in the late 8-minute region of the extracts appeared to be a resin acid methyl ester. Previous GC analyses have not, however, shown any major differences in resin acid composition for similar pulping studies.[17] Dehydroabietic, which has been shown to be a product of the reaction of AQ with abietic acid,[18] but not reported in a previous analysis,[17] was detected in all three pulping extracts.

Table 1 gives the tentative assignment of structures to the various components in the methylated soda/AQ liquor extract (cross reference the EI reconstructed chromatogram in Fig. 3). The methylation procedure efficiently transformed carboxylic acids to esters but left some phenolic components unmethylated. The major components in the extracts were fatty and resin acids and vanillin. Anthraquinone, which was used in the soda/AQ cook at a 0.1% level based on wood, was only visible in the EI chromatogram after ion profiling the *m/e* 208 ion (AQ molecular ion); it just preceded the large methyl oleate signal in the soda/AQ extract. The small

Table 1

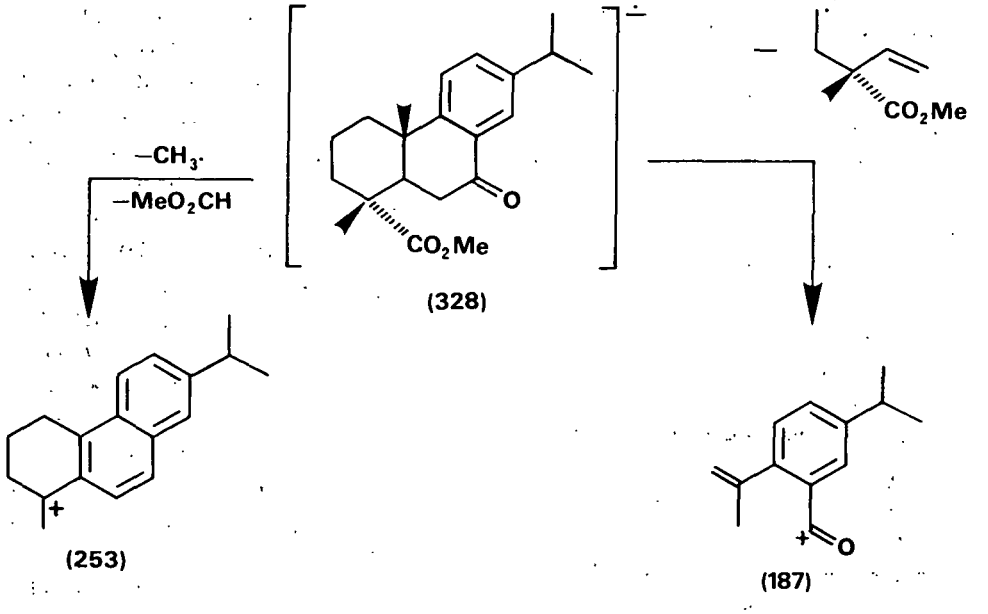
Soda/AQ Methylated Liquor Extract EI Mass Spectral Data

Retention Time, min	Relative Peak Ht.[a]	Assignment[b]	Assign Basis[c]	Significant Signals *m/e* (%)	
				Md[d]	Fragments[e]
0.6	1	Methyl cinnamate (?)	F	162(50)	131(100), 103(63), 77(57)
0.8	1	1-(3',4'-Dimethoxyphenyl)-1-ethanol	F	182(3)	164(100), 167(94), 711(5), 151(35)
1.0	1	1-(4'-Hydroxy-3'-methoxyphenyl)propene	L	164(100)	149(29), 131(22), 103(20), 77(19)
1.2	5	3,4-Dimethoxybenzaldehyde	L	166(100)	165(65), 95(26), 77(26), 151(12)
1.8	2	Methyl* and unsubstituted acetovanillone	L	166(42)	151(100), 165(67)*, 180(27)*, 123(23)
2.1	1	1-(4'-Hydroxy-3'-methoxyphenyl)-2-propanone	L	180(25)	137(100), 122(15), 77(10), 94(10)
2.5	1	C_{14}-FAME	L	242(8)	165(100), 151(77), 74(67), 87(40)
4.6	1	1-(4'-Hydroxy-3'-methoxyphenyl)-2-propanol	F	182(46)	137(100), 138(37), 122(14)
4.8	1	C_{16}-FAME (1DB)	F	268(9)	151(100), 55(90), 69(75), 74(70)
5.2	2	C_{16}-FAME	L	270(17)	74(100), 87(62), 143(13), 227(10)
6.0	1	Dibutyl phthalate	L	278(1)	149(100), 91(11), 223(8), 205(8)
6.2	1	C_{17}-FAME	L	284(30)	74(100), 87(72), 55(30), 241(20)
6.7	1	Anthraquinone	L	208(100)	180(70), 152(43), 76(30)
7.3	5	C_{18}-FAME (1DB) - methyl oleate	L	296(13)	55(100), 74(86), 69(84), 83(76)
7.7	1	C_{18}-FAME	L	298(30)	74(100), 87(72), 75(31), 255(17)
7.9	3	C_{18}-FAME (2DB) - methyl linoleate	L	294(40)	67(100), 81(97), 95(59), 82(56)
8.4	2	Methyl pimarate[h]	L	316(15)	121(100), 180(25), 91(18), 257(18)
9.1	4	Methyl resinate[i]	F	316(72)	301(100), 241(71), 149(34), 257(18)
9.4	4	Methyl dehydroabietate	L	314(20)	239(100), 299(22)
9.8	4	Methyl abietate and dehydrodehydroabietate[f]	L,F	316(100)	256(83), 241(65), 257(34), 213(32)
10.1	2	Methyl neoabietate	L	316(59)	135(100), 121(26), 148(23), 237(10)
10.7	2	Methoxy substituted resin acid ester (?)	F	346(7)	303(100), 259(46), 329(44), 121(29)
11.3	1	Dioctyl phthalate	L	390(-)[g]	149(100), 167(37), 279(22), 57(17)
11.7	1	Methyl dehydroabietate-9-one	F	328(39)	253(100), 289(18), 187(15), 270(12)
12.2	1	Methyl ketoabietate-type ester	F	330(41)	255(100), 289(17), 315(12)
13.2	1	Methyl ketoabietate-type ester	F	330(41)	255(100), 316(11), 315(11)
15.4	1	Cis-3,3',4,4'-tetramethoxystilbene	F	300(100)	285(67), 96(28), 124(27), 176(26)
16.1	1	Trans-3,3',4,4'-tetramethoxystilbene	F	300(100)	285(64), 281(43), 161(37), 269(20)
18.3	1	4,4'-Dihydroxy-3,3'-dimethoxystilbene	F	272(100)	211(9), 168(7)
30.9	1	β-Sitosterol (?)[j]	F	414(100)	81(97), 107(93), 131(90), 121(80)

[a]Relative peak height from 1 to 5, with 5 being full scale.
[b]The abreviations are C_n = number of carbons, DB = double bonds, and FAME = fatty acid methyl ester.
[c]The symbol L means a library fit at the 98% or better confidence limit, and the symbol F means based on interpretation of fragmentation pattern, which does not necessarily have a high degree of confidence.
[d]The apparent molecular weight, generally reinforced by the CI spectrum.
[e]Signals which appear to be only C-13 (P + 1) isotope extensions of major ions are not included.
[f]Minor signal at *m/e* 312.
[g]Not seen in the EI spectrum, but strong 391 (M + 1) in the CI spectrum.
[h]The signal at *m/e* 91 might be indicative of methyl palustrate, which is known to have an intense signal here.
[i]The spectrum was not an excellent fit to any resin acid ester; therefore, this signal may be due to a combination of resinates, such as isopimarate, sandaracopimarate and palustrate;
[j]A pure sample of nonmethylated β-sitosterol had a retention time of 50 minutes and *m/e* 414 of 38% of the base peak at 43.

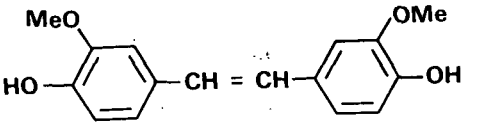
amounts of phthalates observed in cook samples were probably due to contaminants introduced during the workup procedures.

Several suspected ketonic (oxidized) resin acid methyl esters (*m/e* 328 and 330) were observed in all the liquor extracts. The assignment of these structures was based on similarities of fragmentation patterns to other resin acids.[19] The ketone of methyl dehydroabietate is believed to fragment in the following way to give the observed *m/e* signals at 253 and 187:

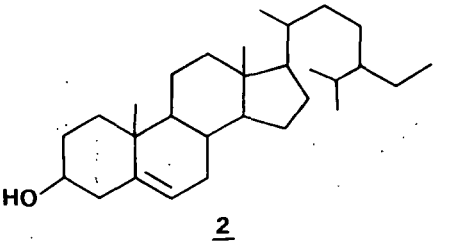


Both methylated and nonmethylated liquor extracts from each cook contained two components displaying strong, apparent molecular ion signals at *m/e* 272. This is typical of stilbenes,[20] a common minor component of pulping liquors.[21] The cis and trans isomers of stilbene (1) have been assigned to these two components. The long retention time component, with an apparent molecular ion signal at *m/e* 414, may be due to β-sitosterol (2), the major neutral in tall oils.[22] The structures assigned to the lignin components were based on the expected strong signal due to benzyl ions resulting from C_α-C_β cleavage (3).[23]

The NCI GC-MS analysis of the methylated strong liquor extracts of the three cook samples produced the data shown in the bottom reconstructed chromatograms of Fig. 1-3. Not only do the



1



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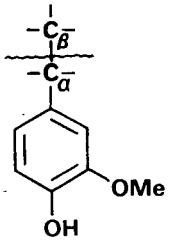


3

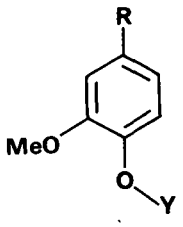
three NCI chromatograms not resemble each other, they do not resemble their own EI and CI chromatograms. The latter effect is a consequence of the NCI mode's lack of response to weakly electrophilic components, namely, resin and fatty acids and simple lignin fragments.

Actually, the signals observed in the first few minutes of the soda and soda/AQ chromatograms were due to lignin fragments, intensified by a reaction of chloride ion from the trailing $CHCl_3$ solvent. A technique for sensitizing compounds to give good NCI responses is to use a MS reagent gas, such as methylene chloride or freon, which transfers chloride ion to the sample, resulting in strong M + Cl signals [Eq. (2)].[24,25] The residual chloroform eluting in the first few minutes of our GC-MS runs functions in a similar way.

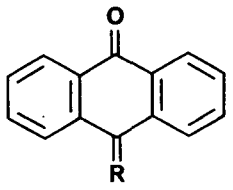
$$\text{Compound (M)} + {}^{35,37}Cl^- \longrightarrow (M + {}^{35}Cl)^- + (M + {}^{37}Cl)^- \quad (2)$$

Several known samples were analyzed by NCI GC-MS, with and without the presence of $CHCl_3$ as the solvent. Invariably, when the compound eluted shortly after the solvent $CHCl_3$ there were intense signals corresponding to the compound's molecular weight plus ^{35}Cl and ^{37}Cl. In the absence of $CHCl_3$ (and even minor amounts in the presence of $CHCl_3$), vanillin (4), vanillyl alcohol (5), methyl vanillyl alcohol (6), acetovanillone (7), eugenol (8), and 3,4-dimethoxyphenethanol (9) showed substantial M-1 signals and variable intensity molecular ion signals in the NCI. On the

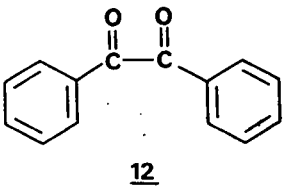
other hand, anthrone (10), anthraquinone (11), benzil (12), and compound 13[26] gave only one signal - that corresponding to the molecular weight. Vanillyl alcohol condensation products, such as 14,[27] did not respond to NCI.



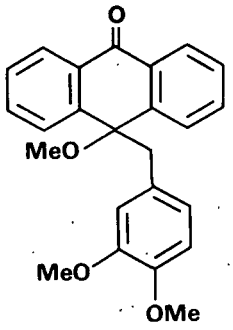
4, Y =H, R = CHO
5, Y =H, R =CH_2OH
6, Y = Me, R = CH_2OH
7, Y = H, R = COMe
8, Y = H, R = $CH_2CH{=}CH_2$
9, Y = Me, R = CHOHMe



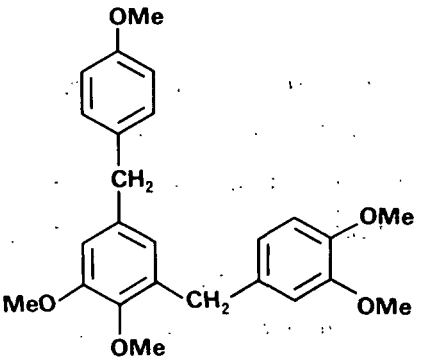
10, R = H, H
11, R = O



12



13



14

The aromatic models examined by NCI were not very responsive unless activated by extended conjugation, attached carbonyl groups, or Cl^- from the solvent. Besides the occurrence of M, M-1, and M + Cl signals noted above, the spectra also showed vanillyl alcohol, *m/e* 136 (base peak, M-water); eugenol, *m/e* 162 (30%, M-2); 3,4-dimethoxyphenethanol, *m/e* 150 (100%, M-32), 165 (28%, M-17) and 166 (26%, M-16); adduct 13, *m/e* 342, 343, and 344 (~ 6%, M-32, 31, and 30).

The intensities of the responses in the soda NCI GC-MS reconstructed chromatograph (Fig. 1) are misleading. The computer program used to generate the chromatogram normalizes on the most intense signal. Thus, even a sample with overall weak NCI responses will have an apparent intense signal, but only because

of the nature of the computer printout. The two large signals in the early minutes of the soda NCI run were vanillin and acetovanillone. The series of smaller signals, beginning at 5.4 minutes, was due to resin and fatty acid methyl esters. Selective ion monitoring of *m/e* 148 revealed that small quantities of phthalates were probably present.

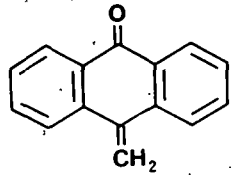
The kraft methylated liquor extract provided an unusual NCI chromatogram, consisting of two intense, broad signals, one centered at 1.5 minutes and the other at 5.0 minutes (Fig. 2). Both signals displayed strong *m/e* 96 and 128 signals indicative of S_3^- and S_4^-. The 5.0-minute component(s) had a regular pattern of ions differing by 32 units, i.e., 96, 128, 160, 192, and 224 (base peak) indicative of S_{3-7}^-. The 1.5-minute component(s) had, besides 96 and 128 ions, weaker signals at several mass units not corresponding to multiples of sulfur. Spectra recorded over the widths of each of the two broad signals were similar, but not identical, to neighboring scans. Thus, it appears that the kraft liquor NCI GC-MS analysis is highly sensitive to sulfur components and that several forms of sulfur exist here.

Elemental sulfur (S_8, mol.wt. 256) was observed as a weak signal in the EI analysis of the kraft liquor at a retention time of 4.7 minutes. Therefore, the signal at roughly 5.0 minutes in the NCI analysis was probably sulfur, and the observed ions were fragments thereof. It appears that NCI could be used as a powerful detector for sulfur components in pulping systems. Again, selective ion monitoring of the NCI chromatogram for *m/e* 148 (phthalates) showed only very minor amounts.

The methylated soda/AQ liquor NCI chromatogram (Fig. 3) displayed a large AQ signal at 7.2 minutes. Keeping in mind that AQ is only a very minor component in the sample (as shown by the EI chromatogram), we believe that NCI could be useful for the analysis of trace levels of AQ in pulping and bleaching products and effluents. Selective ion monitoring of *m/e* 148 showed that the second most intense signal (11.8 minutes) and the one at 6.5

minutes probably represent phthalate contaminants (Fig. 4). The two phthalate components were assigned structures based on the EI spectra of components of similar retention times (Table 2). Phthalates, like AQ, are electron-deficient aromatics that should readily accept electrons to become negatively charged ions.

The early signals in the NCI chromatogram of the soda/AQ liquor extract have been assigned to vanillin and acetovanillone and their methylated analogs. The three obvious signals in the 8-11 minute region were tentatively identified as AQ derivatives 15-17. The *m/e* 208 ion present in the 9.0-minute signal may be due to 10-methylanthrone (19) or a natural fragment ion.



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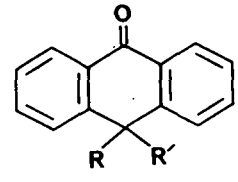

16, R = H, R′= CH_2OH
17, R = H, R′= CHO
18, R = OH, R′= CHO
19, R = H, R′= CH_3

The basis for the structural assignments of 15-17 was (a) the apparent molecular ions, which were strong signals, as NCI predicts;[16] (b) the signals were peculiar to the AQ cook, suggesting they were AQ by-products; (c) the structures were expected to be NCI sensitive; (d) the logic that 17 was an aldehyde, since it displayed a strong M-1 ion, similar to vanillin, and (e) the expectation, based on the literature, that these compounds would be present. A surprise was the apparent lack of any anthrahydroquinone-quinonemethide adducts in the sample. [The adduct 13[27] was shown to elute at 18.5 minutes under the GC conditions used in the extract analyses and to be quite responsive to NCI.] Adducts may have been absent because they were not (a) formed during pulping or (b) extracted during sample workup. Benzanthrones[28,29] were not observed, possibly for the same reasons.

Table 2

Soda/AQ Methylated Liquor Extract NCI MS Data

Min.	Ht.[a]	Assignment (mol.wt.)	Significant Signals, *m/e*, (%)[b]
0.6	1	Unknown	162(100), 184(12), 138(11), 196(9)
0.9	1	Residual components[c]	208(100), 206(20), 192(18), 214(4)
1.5	2	Vanillin (152)[d]	151(100), 187/189(70), 152(36)
2.2	2	Acetovanillone	201/203(100), 180(56), 165(47)
6.5	2	Dibutylphthalate (278)	148(100)[f]
7.3	5	Anthraquinone (208)	208(100)[f]
8.6	1	10-Methylene-9-anthracenone (200)	206(100)[f]
9.0	2	10-Hydroxymethyl-9-anthracenone (224)	224(100), 206(94), 208(25), 207(19)
10.1	2	10-Formyl-9-anthracenone (222)	221(100), 148(20)[f]
11.8	3	Dioctyl phthalate (390)	148(100), 278(6)[f]
12.4	2	Unknown (274)	273(100)[f]
13.6	1	Unknown (274)	274(100), 318(54), 299(21), 300(16)

[a]Relative peak height from 1 to 5, with 5 being full scale; [b]#/# + 2 Signifies a 3:1 chlorine pattern; [c]Suspect these components were carried through rapidly with solvent; [d]Also methyl vanillin present: 165(30), 166(17), 201(7)(M + Cl); [e]Also methyl acetovanillone: 180(56), 179(18); [f]No other signal greater than a few %.

Both 10-methylene[4,30] and 10-methylanthrone[30] (15 and 19) have previously been shown to be present in AQ pulping liquors. The latter compounds methyl group apparently comes from the reducing carbon of carbohydrates since glucose labeled at C-1 with carbon-14 gave 10-(^{14}C)-methylanthrone.[30] A likely reaction sequence to give the 10-methyl derivative is initial production of 18 from AHQ and carbohydrates, followed by a series of reductions, 18 ⟶ 17 ⟶ 16 ⟶ 15 ⟶ 19. The NCI mass spectrum of the soda/AQ liquor extract has apparently confirmed the presence of the missing intermediates 16 and 17.

Several attempts to synthesize 10-formylanthrone (17), including the use of a published procedure for 17,[31] were not successful. We had hoped to compare the NCI spectra and retention time of an authentic sample of 17 and its reduction product 16 to those of the components present in the soda/AQ extract.

The soda/AQ pulp extract was also analyzed by NCI. This is shown in Fig. 5, together with the EI and CI results. Again, the NCI reconstructed ion chromatogram was substantially different from the EI and CI chromatograms. Table 3 presents the revelant NCI spectral data and assignments of component structures. The only AQ derivative observed here was 10-hydroxymethylanthrone (16, 8.7 min). Since NCI spectra were not recorded for the other pulp samples, it is not known if the substantial signals at 3.4 and 5.9 min were peculiar to the soda/AQ process.

Table 3

Soda/AQ Methylated Pulp Extract NCI MS Data

Min	Ht.[a]	Assignment (mol.wt.)	Significant Signals, *m/e*, (%)[b]
1.5	5	Vanillin (152)	187/189(100), 151(100), 171(14)
3.4	5	Unknown	122(100), 155(28), 154(10), 124(4)
4.9	1	Unknown phthalate	148(100), 155(9), 162(4), 119(3)
5.9	4	Unknown	140(100), 122(52), 155(49), 138(48)
6.1	4	Dibutyl phthalate (278)	148(100)[c]
7.0	3	Anthraquinone (208)	208(100)[c]
8.7	2	10-Hydroxymethyl-9-anthracenone (224)	206(100), 224(90), 208(17), 209(8)
11.4	2	Dioctyl phthalate (390)	148(100), 184(16), 329(6)
12.1	2	Unknown	339(100), 273(46), 314(13), 151(12)
14.3	1	Unknown	315(100), 316(25), 184(10), 340(7)
15.2	2	Unknown	361(100), 329(6), 334(4)
15.7	2	Unknown	334(100), 346(58), 310(13), 344(12)

[a]Relative peak height from 1 to 5, with 5 being full scale; [b]#/# + 2 Signifies a 3:1 chlorine pattern; [c]No other signal greater than a few %.

CONCLUSIONS

The application of various types of GC-MS analyses of pulps and pulping liquor extracts has proven useful in detecting some interesting, minor components, such as oxidized resin acids, lignin fragments, sulfur, AQ, and AQ by-products. The technique of NCI is particularly sensitive to the presence of sulfur, AQ and AQ by-products and may prove to be very beneficial to future analytical studies of kraft and additive pulping systems.

EXPERIMENTAL

The GC-MS instrumentation and conditions have been previously described[27] except for the NCI mode which used methane as the GC carrier gas directly into the isatron, with an ionizing voltage of 230 eV and a mass scan range of 50-700 amu. The pulping procedures giving rise to 30 $\pm$ 2 kappa number pulps, along with the liquor extraction and methylation (diazomethane) procedures, have also been previously described.[18] The "methylated pulp extracts" were obtained by: (a) extracting an approximate 8-g pulp sample in a Soxhlet extractor with chloroform for 1 day, (b) evaporating the $CHCl_3$ solution, and (c) methylating (diazomethane) a portion of the resulting $CHCl_3$ residue.

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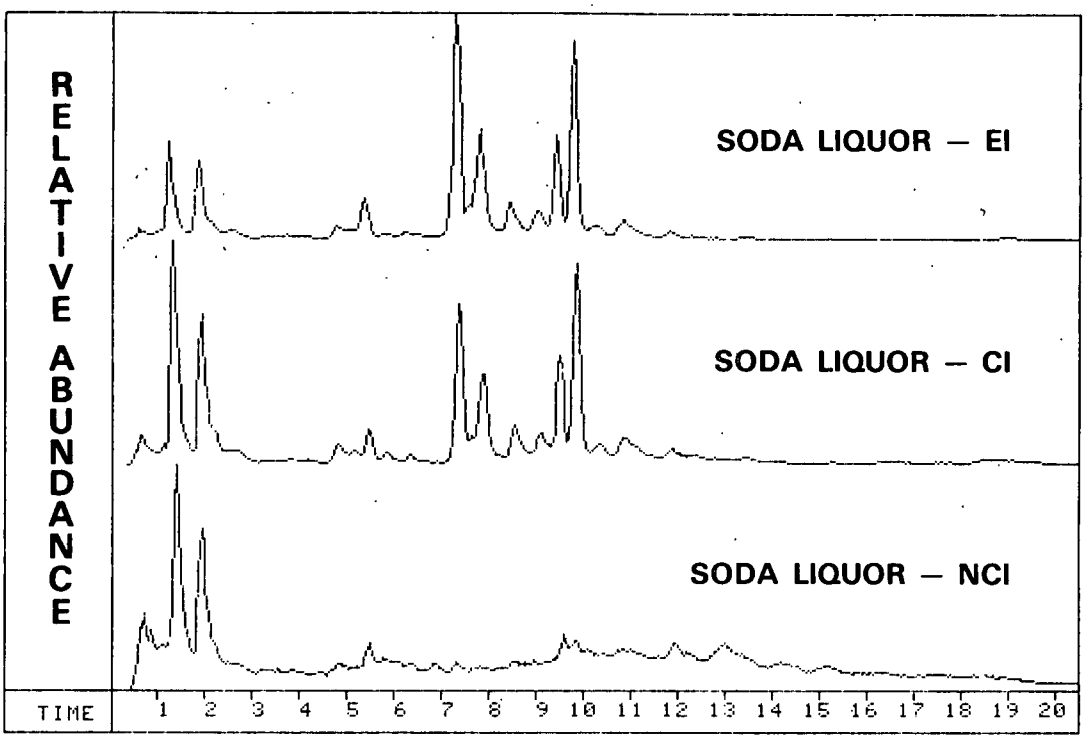

Figure 1. Reconstructed Total Ion Chromatograms of Methylated Loblolly Pine Soda Liquor Extract in Three MS Modes; Time in Minutes

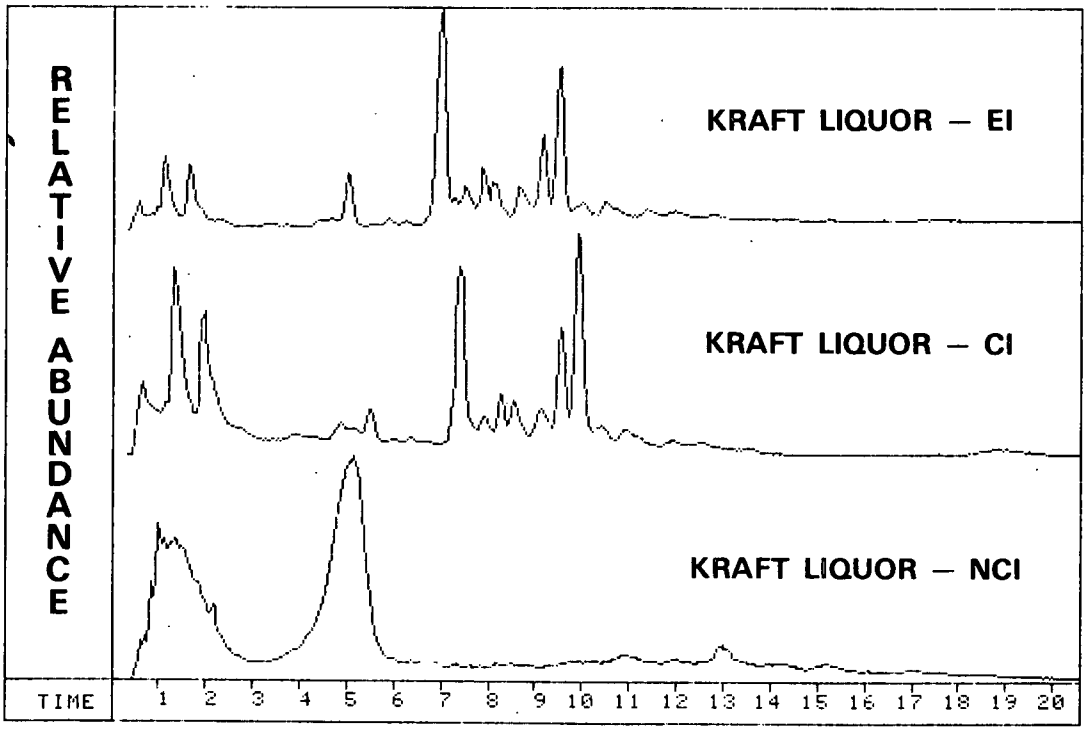

Figure 2. Reconstructed Total Ion Chromatograms of Methylated Loblolly Pine Kraft Liquor Extract in Three MS Modes; Time in Minutes

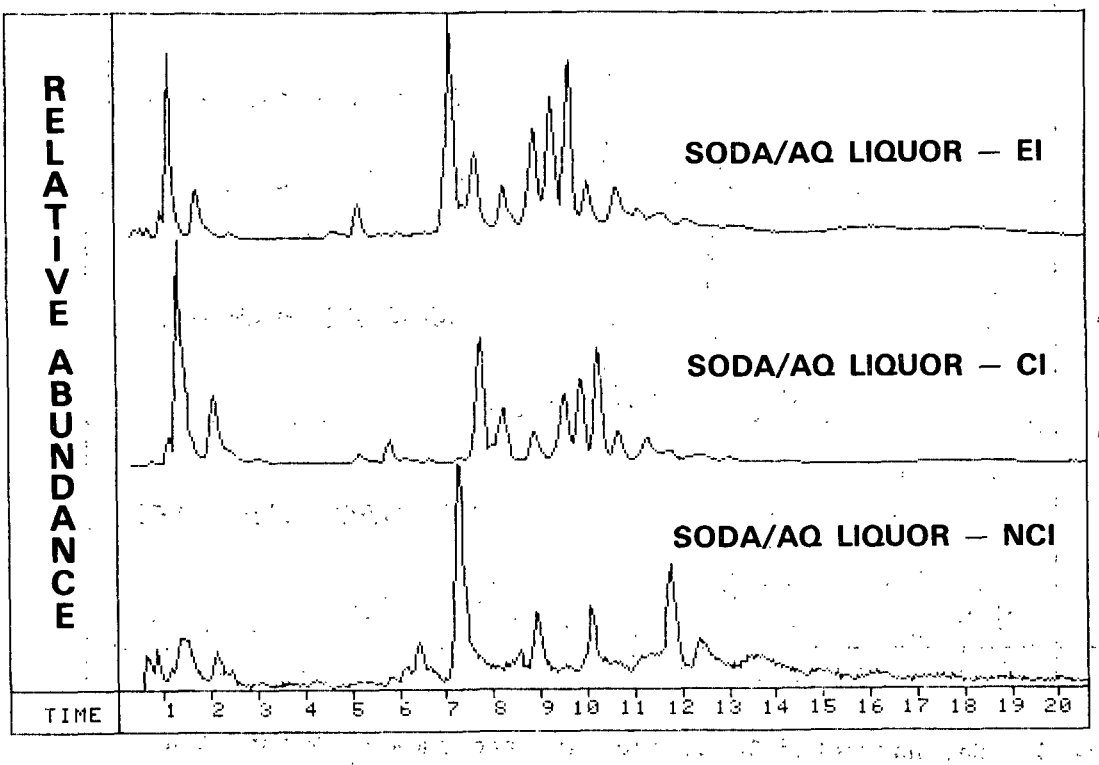

Figure 3. Reconstructed Total Ion Chromatograms of Methylated Loblolly Pine Soda/AQ Liquor Extract in Three MS Modes; Time in Minutes

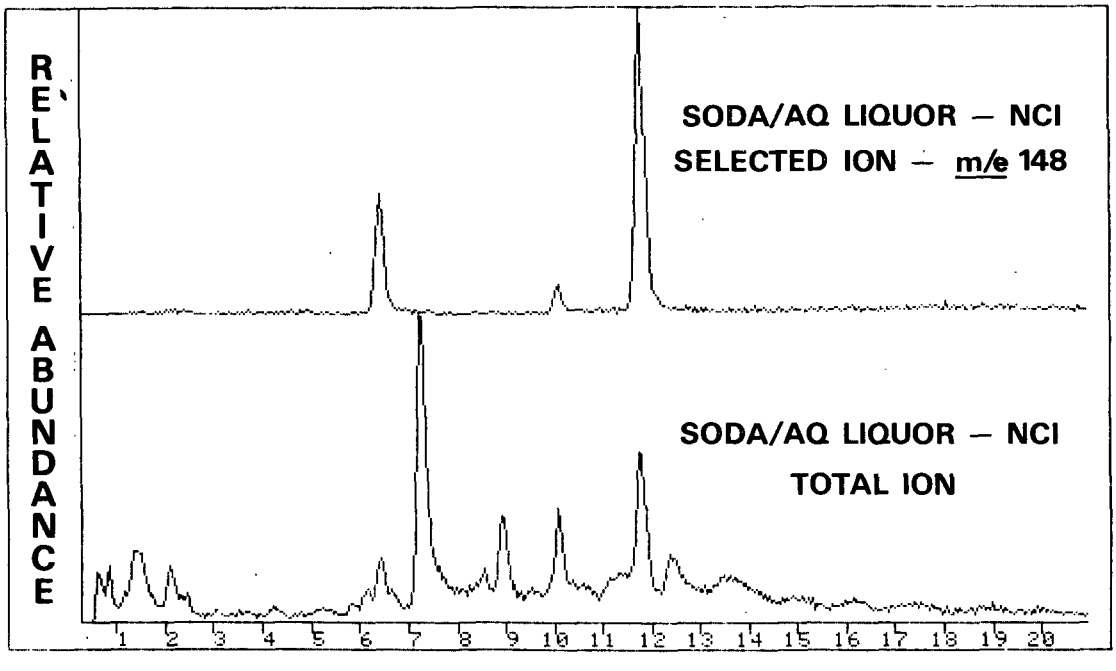

Figure 4. Reconstructed Selected (*m/e* 148) and Total Ion Chromatograms of Methylated Soda/AQ Liquor Extract in the NCI Mode; Time in Minutes

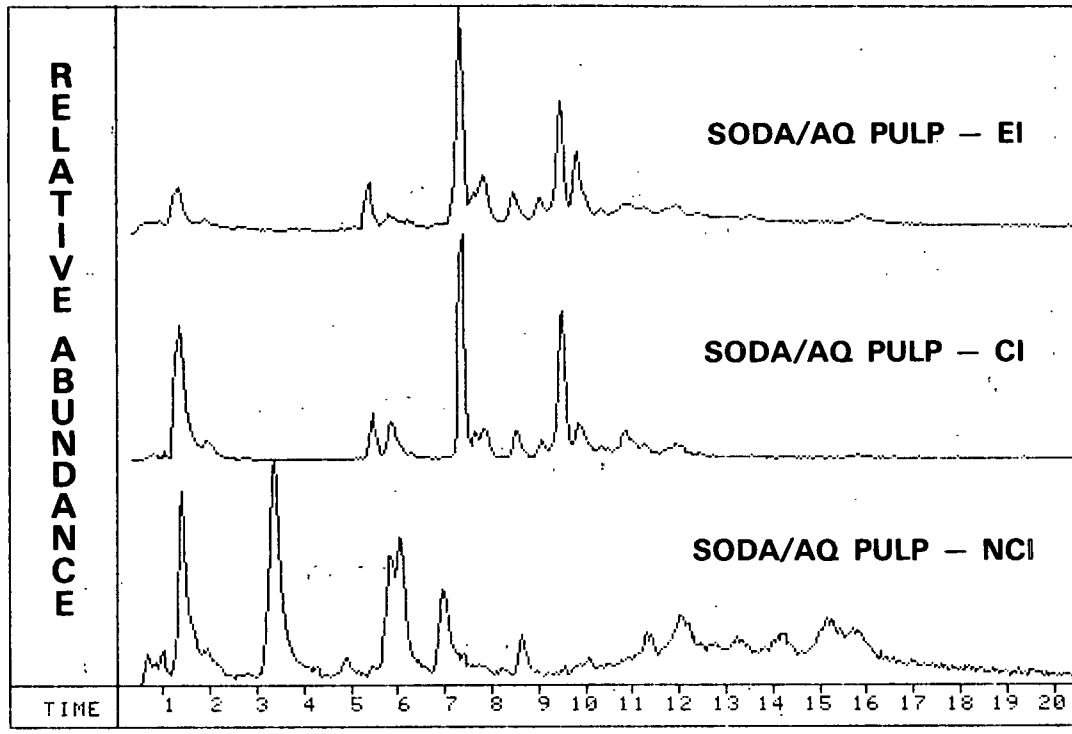

Figure 5. Reconstructed Total Ion Chromatograms of Methylated Loblolly Pine Soda/AQ Pulp Extract in Three MS Modes; Time in Minutes